GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

Date: 5 March 1969

RESEARCH PROJECT INITIATION

Project Title: Electronic Spectra of Porphyrin Cations

Project No.: B-1534

Project Director: Dr. Ronald H. Felton

Sponsor: Frederick Gardner Cottrell grant in aid, Research Corporation

Agreement Period: From 15 February 1969 until 14 February 1970

Type Agreement: Letter dated February 3, 1969

Amount: $4,780 Capital Outlay (B-1534)
900 Summer Fellowship (R-453)
$5,680 Total Grant

Grant Administrator

Mr. Kendall W. King
Assistant Vice President - Grants
Research Corporation
405 Lexington Avenue
New York, N. Y. 10017

Reports Required

Brief Letter - when warranted

Reprints - as they occur

Final - upon completion of project.

Assigned to: School of Chemistry

COPIES TO:

- [X] Project Director
- [X] School Director
- [X] Dean of the College
- [X] Administrator of Research
- [X] Associate Controller (2)
- [X] Security-Reports-Property Office
- [X] Patent Coordinator
- [X] Library
- [X] Rich Electronic Computer Center
- [ ] Photographic Laboratory
- [ ] EES Machine Shop
- [ ] EES Accounting Office

Other Mr. R. A. Martin
File B-1534

REPORTS
300. B-1534
(School)

RA-3 (4/65)

Reports Vol 6
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GEORGIA INSTITUTE OF TECHNOLOGY

OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT TERMINATION

Date: September 19, 1973

Project Title: "Electronic Spectra of Porphyrin Cations"

Project No: G-33-608

Principal Investigator: Dr. Felton

Sponsor: Research Corporation

Effective Termination Date: September 17, 1973

Clearance of Accounting Charges: All charges are clear

COPIES TO:

Principal Investigator
School Director
Dean of the College
Director of Research Administration
Associate Controller (2)
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Library, Technical Reports Section
Rich Electronic Computer Center
Photographic Laboratory
Terminated Project File No. G-33-608
Other _____

RA-4 (5/70)

G-33-608

REPORT OF RESEARCH CORPORATION GRANT

(Please check one)
(Submit original and one legible copy)

☐ Interim Report
☒ Terminal Report

INSTITUTION AND ADDRESS Georgia Institute of Technology, Department of Chemistry, Atlanta, Georgia 30332

PRINCIPAL INVESTIGATOR RONALD H. FELTON PHONE 404 - 894-4013

ACADEMIC RANK AND DEPARTMENT Associate Professor of Chemistry

SHORT TITLE OF RESEARCH SUPPORTED BY GRANT

Electronic Spectra of Porphyrin Cations

STARTING DATE 2/15/69

SUMMARY OR PRINCIPAL FINDINGS AND THEIR SIGNIFICANCE (State succinctly in language understandable to one not necessarily expert in this field. Include extent to which original goals have been realized and any changes to original plan made or contemplated.)

The cyclic tetrapyrrole denoted as porphyrin (I) complexes a variety of divalent and trivalent metals. Cyclic voltammetry showed in many instances that the porphyrin ring rather than the metal was oxidized at the electrode. Preparative electrochemistry afforded bulk amounts of the isolable electrode products. Their characterization was accomplished by observation of hyperfine structure (hfs) in the epr spectrum, optical spectra and chemical reactions. Table I summarizes some of our findings.

TABLE I

Metal	Porphyrin	Ions	Epr	Remarks
Zn	TPP	+1, +2	hfs	+2 reacts with nucleophilles to form isoporphyrins
Zn	OEP	+1, +2	singlet	+1 dimerizes
Mg	TPP	+1, +2	hfs	isoporphyrin formed
Mg	OEP	+1, +2	hfs	+1 dimerizes
Cl	TPP	+1	hfs	-
Ag	TPP	+1	-	Ag(III) formed
Co(II)	TPP	+1, +2	Co hfs	Co(III), $Co(III)P^{+\cdot}$ formed
Co(III)	OEP	+1, +2	Co hfs	Co(III), $Co(III)P^{+\cdot}$ formed
Fe(III)	TPP	+1	no epr	Fe(IV) formed
Fe(III)	OEP	+1	no epr	Fe(IV) formed
(Fe(III)	$TPP)_2O$	+1	epr	Fe(IV)-O-Fe(III)
(Fe(III)	$OEP)_2O$	+1	epr	Fe(IV)-O-Fe(III)
Fe(III)	mesoporphyrin	+1	no epr	Fe(IV)

STUDENT PARTICIPATION (Give names of students working on the project, their role in the research, their achievements and their career plans.)

1. Dr. G. S. Owen, Research Associate, now Assistant Professor of Chemistry, Atlanta University.
2. Mr. G. Kuipers, Research Assistant, preparation of porphyrin anions.
3. Mr. B. Curry, undergraduate, SCF-theory, now graduate student at Ohio State.
4. Mr. P. Wilson, undergraduate, Huckel theory, now at Eastman Kodak.
5. Mr. H. Kurtz, undergraduate, binding studies, now a graduate student at University of Florida.

PAPERS AND SCIENTIFIC TALKS (Give titles and references to papers or talks resulting from the work. Attach two copies of any reprints available, if not previously forwarded.)

See attached list

OTHER SUPPORT (List amounts and sources—including institutional—of other contributions received or expected for this work.)

1. NSF $70,000
2. NIH $140,000

EXPENDITURE OF RESEARCH CORPORATION GRANT FUNDS (The terminal report should be approved by an authorized officer of the institution.)

a. Equipment, supplies (Itemize major expenditures)

1. Equipment	
a. Potentiostat	2,301
b. PDP-8E memory	900
2. Supplies	2,273

b. Stipends (Academic status, rates, periods of appointment)

1. Part-time student (undergraduate) 10/69 - 12/69	206

c. Other expenditures (Itemize and give purpose)

None

total $5,680

Signature of principal investigator

Milton W. Bennett, Acting Director
Research Administration

Date Sept. 5, 1973

Signature of authorized officer of institution (required for terminal report only)

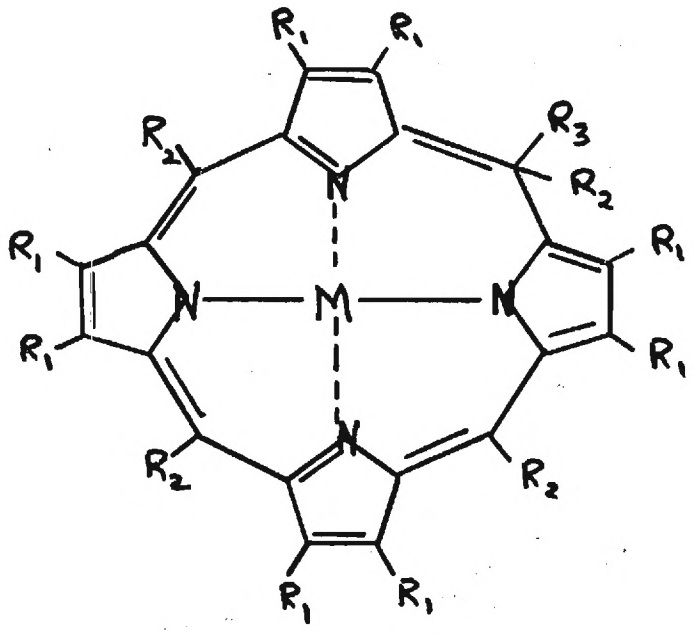
Date Sept 6, 1973

Dr. J. Aaron Bertrand, Director, School of Chemistry, Georgia Institute of Technology
Name and position of authorized officer of institution

Extension of these techniques to Chlorophyll and bacteriochlorophyll has shown P700 and P865 in photosynthetic reaction centers to be π-cations. Epr data on model bacteriochlorins has permitted tentative assignment of endor lines in the in vivo systems.

Spectral similarities between $Co(III)OEP^{+\cdot}$ and peroxidase complexes led to a suggestion of an $Fe(IV)P^{+}$ species in the enzymatically active hydroperoxidases. This proposal was followed shortly by demonstration of Fe(IV) porphyrins in model systems.

Original goals in this research have been met and are being extended to the physiologically relevant systems.



MTPP (R_1=H, R_2=Ph

MOEP (R_1=C_2H_5, R_2=H)

Isoporphyrin (R_3=OCH_3, OH)

A. Papers resulting from this work

Publications:

1. J. Fajer, D. C. Borg, A. Forman, D. Dolphin, R. H. Felton, J. Amer. Chem. Soc., 95, 2739 (1973).

2. R. H. Felton, G. S. Owen, D. H. Dolphin, J. Fajer, "Iron(IV) Porphyrins," J. Amer. Chem. Soc., 93, 6332 (1971).

3. A. Forman, D. C. Borg, R. H. Felton, J. Fajer, "Hyperfine Interaction of Halide Ions with Metalloporphyrin Cation Radicals," J. Amer. Chem. Soc., 93, 2970 (1971).

4. D. Dolphin, A. Forman, D. C. Borg, J. Fajer, R. H. Felton, "Compounds I of Catalase and Horse Radish Peroxidase: π-Cation Radicals," Proc. Nat. Acad. Sci., 68, 614 (1971).

5. D. Borg, J. Fajer, R. Felton, D. Dolphin, "π-Cation Radicals of Chlorophyll-a," Proc. Nat. Acad. Sci., 67, 813 (1970).

6. J. Fajer, D. Borg, A. Forman, D. Dolphin, R. Felton, "π-Cation Radicals of Metalloporphyrins," J. Amer. Chem. Soc., 92, 3451 (1970).

7. D. Dolphin, R. Felton, D. C. Borg, J. Fajer, "Isoporphyrins," J. Amer. Chem. Soc., 92, 743 (1970).

In Press:

1. R. Felton, G. Owen, D. Dolphin, J. Fajer, A. Forman, and D. Borg, "Oxidation of Ferric Porphyrins," Ann. N.Y. Acad. Sci., 000 (1973).

2. J. Fajer, D. C. Borg, A. Forman, R. Felton, L. Vegh, D. Dolphin, "ESR Studies on π-Cations: $^2A_{1u}$ and $^2A_{2u}$ States," ibid, 000 (1973).

3. D. Dolphin, Z. Muljiani, K. Rousseau, D. Borg, J. Fajer, R. Felton, "Chemistry of Porphyrin π-Cations," ibid, 000 (1973).

4. D. Dolphin and R. H. Felton, "The Biochemical Significance of Porphyrin π-Cation Radicals," Accts. Chem. Res., 000 (1974).

5. J. A. Guzinski and R. H. Felton, "Meso-tetraphenylmethoxyisoporphyrin Iron(III) chloride, Chem. Comm., 000 (1973).

B. Talks

1. Primary Photochemical Events in Photosynthesis, November, 1971, Argonne National Laboratory.

2. New York Academy of Sciences, Conference on Porphyrin Chemistry, April, 1972.

3. Seminars at LSUNO, Clemson and Georgia State.